Nucleophilic Addition to (η^3-Allyl)Fe(CO)$_4$ Cations with Functionalized Zinc-Copper Reagents RCu(ZnI)CN

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Regioselectivity of the addition of the highly functionalized zinc-copper reagents to (η^3-allyl)Fe(CO)$_4$ cationic salts was studied. For 1,1-disubstituted allyl cation **1**, the zinc-copper reagents added predominantly at the unsubstituted terminus. For 1,1,2-trisubstituted allyl cation **2**, reactive zinc-copper reagents attacked mainly at the unsubstituted terminus while less reactive zinc-copper reagents added to a coordinated CO ligand. For 1,1,3-trisubstituted allyl cation **3**, the addition occurred at both the less substituted allyl terminus and a coordinated CO ligand.

INTRODUCTION

Conjugated dienes are generally inert towards nucleophilic addition. Nevertheless, the activation of the dienes can be achieved by complexation with tricarbonyliron.[1] The reactive carbanions can react with (η^4-1,3-diene)Fe(CO)$_3$ to bring about an internal addition at -78 °C as well as a terminal addition at 23 °C.[2] The disadvantage of the addition, however, is the relatively narrow range of nucleophiles (pKa 24-31).[3] For example, organomagnesium or lithium reagents suffer competitive addition to the carbon monoxide ligands. Ketone enolates, organocopper as well as organozinc compounds fail to react with the complexes.[4] Alternatively, (η^4-1,3-diene)Fe(CO)$_3$ complexes can be further activated towards nucleophilic addition by treatment with HBF$_4$ under an atmosphere of CO.[5] The resultant cations, (η^3-allyl)Fe(CO)$_4$ are known to couple smoothly with soft nucleophiles, such as triphenylphosphine, pyridine, malonates, secondary amines, allyl stannes, allyl[FeCp(CO)$_2$] complexes, and electron rich aromatic compounds.[6] For strong nucleophiles, such as organolithiums, organomagnesiums, and allylsilanes, the addition gives mainly the starting complexes, (η^4-1,3-diene)Fe(CO)$_3$.[7] Treatment of the cations with organocuprates resulted in the deprotonation of the starting material.[8] Moreover, organozinc compounds do not react with the cationic salts.[9] Herein we report that the highly functionalized zinc-copper reagents reacted effectively

with (η^3-allyl)Fe(CO)$_4$ cationic salts **1-3** to give a variety of polyfunctionalized isoprenyl derivatives.

RESULTS AND DISCUSSION

(η^3-Allyl)Fe(CO)$_4$ tetrafluoroborates **1-3** were prepared by treatment of the corresponding (η^4-1,3-diene)Fe(CO)$_3$ complexes with HBF$_4$ (48% in H$_2$O) under an atmosphere of CO. The cationic salts were pale yellow powder and handled in the air at room temperature without any precaution. The functionalized zinc-copper reagents were prepared from functionalized alkyl iodides, which were first treated with activated zinc at 40-50 °C under nitrogen for 12 h. The insertion of ethyl 3-iodopropionate and 3-iodopropionitrile was carried out at 23 °C. The functionalized zinc-copper reagents were then generated by transmetallation of the corresponding zinc organometallics with CuCN·2LiCl in THF at -30 °C.[10] The highly functionalized zinc-copper reagents RCu(ZnI)CN (2.5 mol equiv.) in THF was added dropwise to a stirred suspension of cations **1-2** in THF at 0 °C under nitrogen. The addition was carried out for 3 h followed by workup with saturated aqueous ammonium chloride solution and ether extraction. After purification by use of flash column chromatography on silica gel and short-path distillation under reduced pressure (*ca.* 0.02 mmHg), isoprenyl compounds were obtained as major products and a trace amount of ketone adducts (< 5%) as side products. Results of the additions are summarized in Table 1.

The addition occurred predominantly at the unsubstituted terminal position of the allyl group, and polyfunctionalized isoprenyl compounds were generated (pathway a, Scheme I). The formation of a small amount of the ketone adducts could be accommodated by initial addition
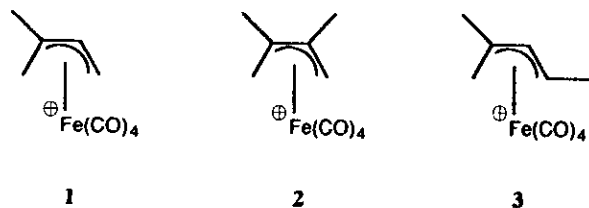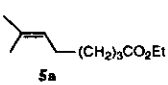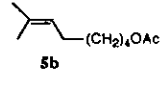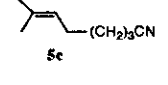
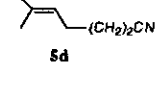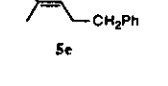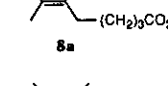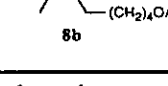|		
$\oplus$ Fe(CO)$_4$	$\oplus$ Fe(CO)$_4$	$\oplus$ Fe(CO)$_4$
1	**2**	**3**

Table 1. Reaction of Cations 1 and 2 with the Functionalized RCu(CN)ZnI Reagents 7a-e

RCu(CN)ZnI	Cation	Products[a,b]	Yield/%
EtO$_2$C(CH$_2$)$_3$Cu(CN)ZnI 7a	1	5a —(CH$_2$)$_3$CO$_2$Et	57[b]
AcO(CH$_2$)$_4$Cu(CN)ZnI 7b	1	5b —(CH$_2$)$_4$OAc	68[b]
NC(CH$_2$)$_3$Cu(CN)ZnI 7c	1	5c —(CH$_2$)$_3$CN	65[b]
NC(CH$_2$)$_2$Cu(CN)ZnI 7d	1	5d —(CH$_2$)$_2$CN	45[b]
PhCH$_2$Cu(CN)ZnI 7e	1	5e —CH$_2$Ph	60
7a	2	8a —(CH$_2$)$_3$CO$_2$Et	53[b]
7b	2	8b —(CH$_2$)$_4$OAc	41[b]

[a] All products were purified by flash column chromatography on silica gel and followed by distillation under reduced pressure. All new compounds have been fully characterized by ^{1}H and ^{13}C NMR, IR, MS, and high resolution mass spectra.

[b] A trace amount (< 5%) of ketone 6 was also isolated.

Table 2. Reaction of Cation 3 with the Functionalized Zinc-Copper Reagents

entry	RCu(CN)ZnI	products[a]	
1	R = EtO$_2$C(CH$_2$)$_3$- 7a	9a —(CH$_2$)$_3$CO$_2$Et 28%	10a —(CH$_2$)$_3$CO$_2$Et 23%
2	R = AcO(CH$_2$)$_4$- 7b	9b —(CH$_2$)$_4$OAc 20%	10b —(CH$_2$)$_4$OAc 20%
3	7b	15%[b]	43%[b]
4	R = PhCH$_2$- 7e	9c —CH$_2$Ph 58%	

[a] All products were purified by flash column chromatography on silica gel, followed by distillation under reduced pressure. All new compounds have been fully characterized by ^{1}H and ^{13}C NMR, IR, MS, and high resolution mass spectra.

[b] The reaction mixture was stirred at -10 °C instead of the regular temperature (0 °C).

of zinc-copper reagents to a coordinated carbon monoxide ligand to produce a metal-acyl intermediate 4. Migration of the acyl group to the unsubst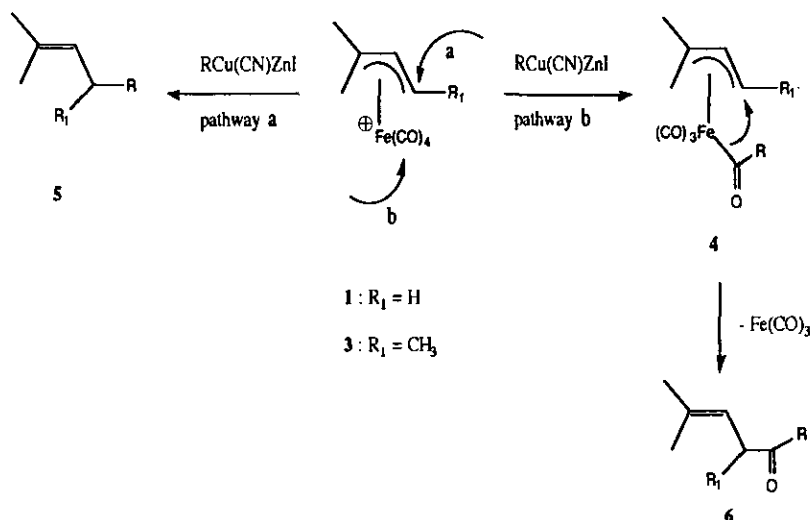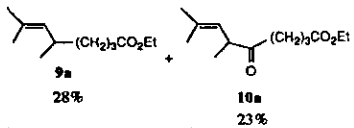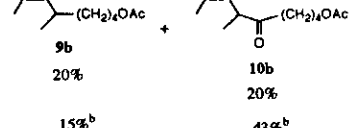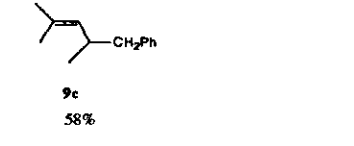ituted terminus (R_1 = H) of the allyl group followed by detachment of the ironcarbonyl moiety from the alkene ligand produced functionalized β,γ-unsaturated ketone 6 (pathway b, Scheme I). Under the same reaction conditions, the addition of the zinc-copper reagents to the 1,1,3-trisubstituted allyl cation 3 gave the usual alkene adducts together with approximately an equal ammount of the β,γ-unsaturated ketones (entries 1 and 2, Table 2). The steric congestion at the terminus of the allyl cation 3 may play an important role in the formation of the

Scheme I

1 : R_1 = H

3 : R_1 = CH$_3$

ketones. We believe that nucleophilic addition at the substituted terminus of the allyl cation 3 was low. The zinc-copper reagents could then attack at a coordinated CO ligand to form an acyl intermediate 4 (R_1 = CH_3). Then, detachment of the ironcarbonyl moiety gave the β,γ-unsaturated ketones.

Moreover, examined the possibility of increasing the yields of ketones by addition of $BF_3 \cdot Et_2O$ or carbon monoxide to the reaction. The result did not show any significant change. Nonetheless, the yields of the ketone adducts increased when reactions were performed at -10 °C (entry 3, Table 2). For the most reactive benzylic zinc-copper reagent, the alkene adduct was the only product isolated either at 0 °C or -10 °C (entry 4, Table 2). We found that the highly reactive benzylic species was able to attack at the steric hindered allyl teminus even at low temperature. The similar regioselectivity was also observed when the mono-substituted (η^3-allyl)molybdenum acetoxytricarbonyl complex was treated with different activity of nucleophiles.[11] The reactive malonates added to the more hindered but electron deficient C-1 position. Nonetheless, the less reactive 1,3-diketone enolates attacked at the non-substituted allyl terminus. We also found that the addition of the least reactive zinc-copper reagent [NC(CH₂)₂Cu(ZnI)CN] (7d)[12] to cations 2 and 3 followed different reaction pathways. Reaction of 7d with cation 2 gave mainly ketone adduct 11. For cation 3, 7d attacked at the allyl terminus to give isoprenyl derivative 12 and at a coordinated CO ligand to give β,γ-unsaturated ketone 13. The C-3 position of cation 3, although more hindered, is electron deficient. Because of the electronic and steric ef-

fect, reagent 7d could attack at both the less substituted terminal and at a coordinated CO ligand. For cation 2, the C-3 position is not electron deficient and hindered by the adjacent methyl group at C-2. Thus, reagent 7d could only attack at a coordinated CO ligand. The divergence in regioselectivity between different nucleophiles and cationic salts did not appear to stem from a single aspect as shown by different experiments. It woud appear to stem from an intricate balance among reactivity of the zinc-copper reagents, the steric demands of the (η^3-allyl)Fe(CO)₄ cations, the charge distribution in the π-allyl system, and the stability of the resultant olefin as well as the olefin-metal complex.
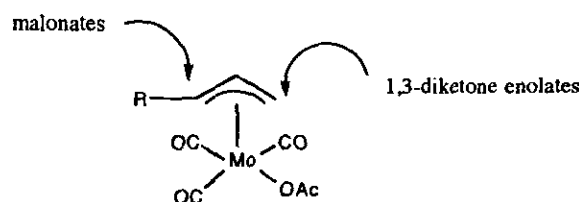
We found that the highly functionalized zinc-copper reagents added smoothly to (η^3-allyl)Fe(CO)₄ cationic salts. The regioselectivity of the addition depended on substituents at the allyl as well as the reactivitiy of the zinc-copper reagents. For the least hindered cation 1, zinc-copper reagents attacked mainly at the allyl terminus to produce isoprenyl adducts. For 1,1,3-trisubstituted allyl cation 3, the regular isoprenyl adducts were isolated together with approximately an equal amount of ketone adducts which were derived from the addition at a coordinated CO ligand.

Scheme II
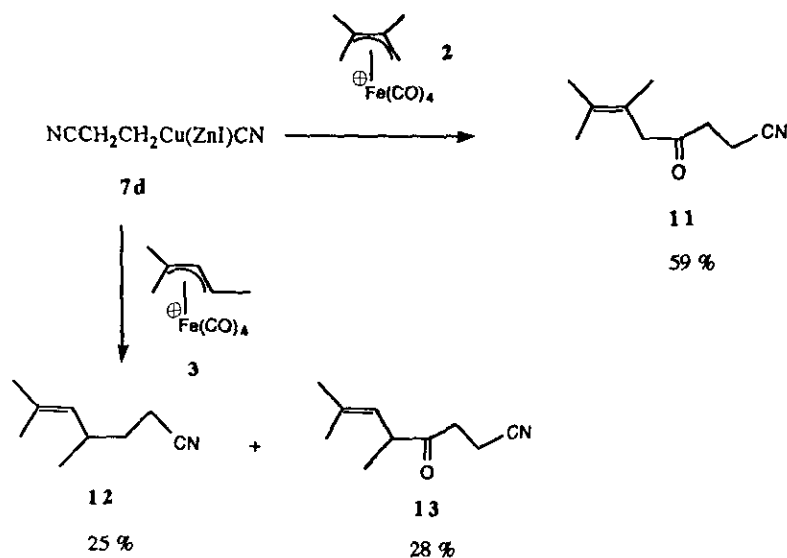
For 1,1,2-trisubstituted allyl cation **2**, the regioselectivity varied with different reactivities of the zinc-copper reagents. Reactive zinc-copper reagents added at the un-substituted allyl terminus and less reactive zinc-copper reagents attacked at a coordinated CO ligand.

EXPERIMENTAL SECTION

Spectra

Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL EX 400 Fourier transform spectrometer and a Bruker AC 200 Fourier transform spectrometer by use of tetramethylsilane or chloroform as an internal standard. The peaks were reported as singlet (s), doublet (d), triplet (t), or quartet (q). Infraed (IR) spectra were measured on a JASCO IR-700. Absorption intensities were recorded as strong (s), medium (m), or weak (w). The 1602 cm^{-1} absorption of polystyrene was used for calibration. Mass spectra were recorded on JEOL JMS-D 100 spectromer. High resolution mass spectra data were obtained on an AEI MS-9 double focusing mass spectrometer and JEOL JMS-HX 110 in the Department of Chemistry, Northern Instrument Center, Hsin Chu.

Chromatography

Flash column chromatography was used to seperate mixtures under positive nitrogen pressure with gradient solvent as eluant. The packing material is Bodman silica gel 60 (230-400 Mesh). Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel-backed plates with a 0.25-mm thickness. Visualization of spots on TLC plate was done by use of UV light or 1% of sulfuric acid and 1% of *p*-anisaldehyde in ethanol.

Reagents and Solvents

Diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl immediately under nitrogen. Isoprene, 2,3-dimethylbuta-1,3-diene, and 2-methyl-1,3-pentadiene were purchased from Aldrich Chemical Co. and distilled before use. Tetrafluoroboric acid (48% in water) was purchased from Aldrich Chemical Co. and used without further purification. Zinc particle (purity >99.9%) was purchased from Merk Co. and used without purification. Diironnonacarbonyl was obtained by photolysis of ironpentacarbonyl in benzene and acetic acid according to the literature procedure.[13]

Generation of (1,1-Dimethyl-η^3-allyl)Fe(CO)$_4$ (1)[14]

(η^4-Isoprene)Fe(CO)$_3$ was prepared from isoprene

(3.0 g, 44 mmol) and Fe$_2$(CO)$_9$[13] (24.2 g, 66 mmol) in ether at reflux for 16 hr. The reaction mixture was filtered through a bed of Celite and the Celite was washed with ether (3 x 30 mL). The combined ethereal solution was concentrated and followed by flash column chromatography of the residue (400 g of silica gel) with hexanes to afford a yellow solution. Flash distillation of the residue gave 4.58 g (22 mmol, 50%) of (η^4-isoprene)Fe(CO)$_3$ complex. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.3 (*dd*, 1 H), 2.2 (*s*, 3 H), 1.8 (*dd*, 1 H), 0.3 (*d*, 1 H), 0.02 (*dd*, 1 H). (η^4-Isoprene)Fe(CO)$_3$ complex (5.72 g, 27.5 mmol) was replaced in a 100 mL Schlenk flask, followed by addition of 12.6 mL (165 mmol) of CF$_3$COOH. The reaction mixture was placed under an atmosphere of CO. Tetrafluoroboric acid (48%, in H$_2$O, 2.6 mL, 41 mmol) was added to the reaction mixture and the reaction was allowed to stir at 23 °C for 30 min. The above procedure was repeated for three times. Excess of ether (*ca.* 100 mL) was poured into the reaction mixture at 0 °C untill yellow solid precipitated. The yellow solid was filtered and washed with 50 mL of ether. Solid was dried under vacuum for 16 hr to give 7.2 g (81%) of cation **1**. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.10 (*s*, 3 H), 7.65 (*s*, 3H), 6.65 (*dd*, 1 H), 5.70 (*dd*, 1 H), 4.30 (*dd*, 1 H).

Generation of (1,1,2-Trimethyl-η^3-allyl)Fe(CO)$_4$ (2)[14]

(η^4-2,3-Dimethyl-buta-1,3-diene)Fe(CO)$_3$ was prepared from 2,3-dimethyl-buta-1,3-diene (3.0 g, 44 mmol) and Fe$_2$(CO)$_9$ (24.2 g, 66 mmol) in ether upon heating for 16 h. The reaction mixture was filtered through a bed of Celite and the Celite was washed with ether (3 x 30 mL). The combined ethereal solution was concentrated and followed by flash column chromatography of the residue (400 g of silica gel) with hexanes to afford a yellow solution. Flash distillation of the residue gave 4.58 g (22 mmol, 50%) of (η^4-2,3-dimethyl-buta-1,3-diene)Fe(CO)$_3$ complex. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 2.18 (*s*, 6 H) 1.72 (*d*, 2 H), 0.10 (*d*, 2 H). (η^4-2,3-Dimethyl-buta-1,3-diene)Fe(CO)$_3$ complex (2.3 g, 10 mmol) was replaced in a 100-mL Schlenk flask, followed by addition of 4.6 mL (60 mmol) of CF$_3$COOH. The reaction mixture was placed under an atmosphere of CO. Tetrafluoroboric acid (48%, in H$_2$O, 3.8 mL, 15 mmol) was added to the reaction mixture and the reaction was allowed to stir at 23 °C for 30 min. The above procedure was repeated for three times. Excess of ether (*ca.* 100 mL) was poured into the reaction mixture at 0 °C untill yellow solid precipitated. The yellow solid was filtered and washed with 50 mL of ether. Solid was dried under vacuum for 16 hr to give 2.2 g (60%) of cation **2**. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.06 (*s*, 3 H), 7.72 (*s*, 3H), 7.54

(s, 3 H), 6.56 (d, 1 H), 5.80 (d, 1 H).

Generation of (1,1,3-Trimethyl-η^3-allyl)Fe(CO)$_4$ (3)[14]

(η^4-2-Methyl-1,3-pentadiene)Fe(CO)$_3$ was prepared from 2-methyl-1,3-pentadiene (3.0 g, 44 mmol) and Fe$_2$(CO)$_9$ (24.2 g, 66 mmol) in ether at reflux for 16 h. The reaction mixture was filtered through a bed of Celite and the Celite was washed with ether (3 x 30 mL). The combined ethereal solution was concentrated and followed by flash column chromatography of the residue (400 g of silica gel) with hexanes to afford a yellow solution. Flash distillation of the residue gave 4.58 g (22 mmol, 50%) of (η^4-2-mehtyl-1,3-pentadiene)Fe(CO)$_3$ complex. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.10 (d, 1 H), 2.14 (s, 3 H) 1.71 (d, 1 H), 1.39 (d, 3 H), 0.86 (m, 1 H), 0.3 (d, 1 H). (η^4-2-Methyl-1,3-pentadiene)Fe(CO)$_3$ complex (6.70 g, 27.5 mmol) was replaced in a 100-mL Schlenk flask, followed by addition of 14.0 mL (180 mmol) of CF$_3$COOH. The reaction mixture was placed under an atmosphere of CO. Tetrafluoroboric acid (48%, in H$_2$O, 2.9 mL, 45 mmol) was added by syringe to the reaction mixture and the reaction was allowed to stir at 23 °C for 30 min. The above procedure was repeated for three times. Excess of ether (*ca*. 100 mL) was poured into the reaction mixture at 0 °C untill yellow solid precipitated. The yellow solid was filtered and washed with 50 mL of ether. Solid was dried under vacuum for 16 h to give 6.0 g (60%) of cation 3. ^{1}H NMR (CDCl$_3$, 200 MHz) δ 8.27 (s, 3 H), 7.89 (s, 3H), 7.20 (d, 1 H), 4.91 (m, 1 H), 4.31 (d, 1 H).

General Procedure for the Preparation of Functionalized Iodides

Sodium Iodide (2.5 mol equiv) was placed in a 250 mL round bottom flask equipped with a refluxing condenser and a magnetic stirrer. Dried acetone (100 mL) was added to the reaction mixture, followed by addition of one mol equiv. of the corresponding functionalized chloride. The mixture was stirred for 12 h to give a pale yellow solution. The reaction mixture was diluted with EtOAc/hexanes (1/3) and the precipitate was filtered. The resultant solution was washed with water (3 x 150 mL), saturated aqueous sodium chloride solution (3 x 150 mL), dried over anhydrous magnesium sulfate (20 g), and then concentrated on a rotary evaporator. The residue was distilled under reduced pressure to give a colorless liquid. The functionalized iodides can be stored under nitrogen over a bed of copper powder (1 g) at 0 °C for a long period of time.

General Procedure for the Preparation of Functionalized Zinc-Copper Reagents[10]

In a 100 mL 3-neck round bottom flask equipped with

an additional funnel, a thermometer, a nitrogen outlet and a magnetic stirrer was placed 1.7 g (26 mmol) of zinc (Merck, 99.9% purity). The system was flashed three times with nitrogen. Tetrahedrofuran (2 mL) was syringed through the additional funnel, followed by addition of 0.2 mL of 1,2-dibromoethane. The reaction mixture was heated to 65 °C with a heat gun for a minute and cooled to 25 °C. The processes were repeated for three times. Chlorotrimethylsilane (0.2 mL) was then added to the reaction mixture at 25 °C. After stirring at 25 °C for 30 min, a solution of the functionalized iodides (25 mmol) in 10 mL of THF was added dropwise to keep the temperature below 35 °C. After the addition was over, the reaction mixture was stirred at 35-40 °C for an additional 12 h (at room temperature for ethyl 3-iodopropionate and 3-iodopropionitrile and at 0 °C for 2 h in the case of benzyl bromide). Usually less than 100 mg of zinc remained in the mixture. A solution of 1.98 g (22 mmol) of CuCN and 1.9 g (44 mmol) of LiCl (predried under reduced pressure) at 150 °C for 1 h) in 22 mL of THF was cooled to -78 °C. The zinc solution prepared above was syringed slowly into CuCN/LiCl solution. The reaction mixture was stirred at 0 °C for 30 min and was ready to use.

General Procedure for Reaction of the Functionalized Zinc-Copper Reagents with (Allyl)tetracarbonyliron Tetrafluroborates (1-3)

The functionalized zinc-copper reagents (2.5 mol equiv) was added via syringe to a suspension of cations 1-3 in 7 mL of THF at 0 °C under argon. The reaction mixture was allowed to stir at 0 °C for 10 h. The reaction mixture was then quenched with saturated aqueous ammonium chloride solution and was diluted with a soultion of 100 mL of a mixture of EtOAc/hexanes (1/2). The resultant solution was washed with water (100 mL x 3), brine (100 mL x 3), dried over anhydrous magnesium sulfate (10 g), and concentrated to give the crude mixture.

Ethyl 7-Methyl-6-octenoate (5a)

The crude mixture obtained from zinc-copper reagent 7a (5.0 mmol) and cation 1 (2.28 mmol) was seperated by flash column chromatography (silica gel) to give 0.21 g (1.30 mmol, 57%) of 5a with hexanes/EtOAc (20/1) as eluant and a small amount (< 5%) of ethyl 8-methyl-5-oxo-7-nonenate derived from the nucleophilic addition of 7a to a coordinated CO ligand of compound 1. Compound 5a was flash distilled under reduced pressure to give a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.10 (t, 1H, J = 5.8 Hz), 4.13 (q, 2 H, J = 7.1 Hz), 2.31 (t, 2 H, J = 3.1 Hz), 2.0 (m, 2 H), 1.72-1.52 (m, 8 H), 1.45-1.21 (m, 5

H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 173.8, 131.6, 124.2, 60.1, 34.4, 29.3, 27.6, 25.6, 24.6, 17.6, 14.2; IR (neat): 3062 (m), 2930 (s), 1727 (s), 1607 (m), 1458 (w), 1422 (m), 1348 (m), 1141 (m), 1067 (s) cm^{-1}. MS (EI) m/z 264 (M$^+$, 18), 178 (2), 167 (100), 152 (13), 128 (4), 115 (5), 97 (7), 69 (11); HRMS m/z 183.1835, Calcd for C$_{11}$H$_{19}$O$_2$ (M-1) 183.1380.

8-Acetoxy-2-methyl-oct-1-ene (5b)

The crude mixture obtained from zinc-copper reagent 7b (5.0 mmol) and cation 1 (2.0 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give 5b. After purification by use of flash distillation under reduced pressure, 5b (0.25 g, 1.36 mmol, 68%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.10 (t, 1 H, J = 5.7 Hz), 4.06 (t, 2 H, J = 6.8 Hz), 2.05 (s, 3 H), 2.0 (m, 2 H), 2.04-1.97 (m, 2 H), 1.69-1.54 (m, 8 H), 1.42-1.32 (m, 4 H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 171.2, 131.5, 124.4, 64.6, 29.4, 28.5, 27.8, 25.7, 25.5, 21.0, 17.6; IR (neat) 3068 (m), 3060 (s), 1729 (s), 1606 (w), 1449 (m), 1428 (m), 1272 (s), 1160 (s), 1043 (m), 910 (m) cm^{-1}; MS (EI) m/z 184 (M$^+$, 1), 124 (100), 109 (99), 83 (35), 61 (20); HRMS m/z 183.1372, Calcd for C$_{11}$H$_{19}$O$_2$ (M-1) 183.1364.

7-Methyl-oct-6-en-1-nitrile (5c)

The crude mixture obtained from zinc-copper reagent 7c (5.0 mmol) and cation 1 (2.28 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give 5c. After purification by use of flash distillation under reduced pressure 5c (0.088 g, 1.48 mmol, 65%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.0 (t, 1 H, J = 5.4 Hz), 2.34 (t, 2H, J = 7.0 Hz), 2.02 (q, 2H, J = 6.95 Hz), 1.69-1.44 (m, 10H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 132.4, 123.3, 119.7, 28.7, 27.0, 25.6, 24.9, 17.6, 17.1; IR (CH$_2$Cl$_2$): 2930 (s), 2864 (m), 2248 (m), 1606 (m), 1426 (s), 1379 (m), 1253 (m) cm^{-1}; MS (EI) m/z 137 (M$^+$, 8), 122 (10), 108 (17), 94 (17), 82 (11), 56 (27), 33 (100); HRMS m/z 136.1133, Calcd for C$_9$H$_{14}$N (M-1) 136.1126.

6-Methyl-hept-5-en-1-nitrile (5d)

The crude mixture obtained from zinc-copper reagent 7d (5.0 mmol) and cation 1 (2.0 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give 5d. After purification by use of flash distillation under reduced pressure 5d (0.11 g, 0.9 mmol, 45%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.05 (t, 1 H, J = 5.8 Hz), 2.30 (t, 2 H, J = 2.4 Hz), 2.1 (q, 2 H, J = 7.0 Hz), 1.76-1.61 (m, 10H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 133.9, 121.8, 119.7,

26.7, 25.6, 25.4, 24.9, 17.6, 16.3; IR (CH$_2$Cl$_2$) 3060 (w), 2966 (s), 2930 (m), 2246 (m), 1448 (s), 1428 (s), 1409 (w), 1055 (w) cm^{-1}; MS (EI) m/z 123 (M$^+$, 6), 69 (16), 40 (97), 32 (70); HRMS m/z 123.1044, Calcd for C$_8$H$_{13}$N (M-1) 123.1048.

2-Methyl-5-phenyl-pent-2-ene (5e)

The crude mixture obtained from zinc-copper reagent 7e (5.0 mmol) and cation 1 (2.0 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give 5e. After purification by use of flash distillation under reduced pressure 5e (0.19 g, 1.2 mmol, 60%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.31-7.16 (m, 5H), 5.17 (t, 1H, J = 7.0 Hz), 2.61 (t, 2H, J = 5.9 Hz), 2.31 (m, 2H), 1.68 (s, 3H), 1.54 (s, 3 H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 142.4, 132.1, 128.4, 128.2, 125.6, 123.7, 36.1, 30.0, 25.7, 17.6; IR (CH$_2$Cl$_2$) 3062 (m), 2970 (m), 2926 (s), 2246 (m), 1602 (m), 1448 (s), 1450 (s), 1379 (m), 1254 (s) cm^{-1}; MS (EI) m/z 160 (M$^+$, 100), 143 (19), 117 (33), 85 (35), 72 (30), 39 (57). HRMS m/z 159.1174, Calcd for C$_{12}$H$_{15}$ (M-1) 159.1174.

Ethyl 6,7-dimethyl-6-octenoate (8a)

The crude mixture obtained from zinc-copper reagent 7a (5.0 mmol) and cation 2 (2.0 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give 8a. After purification by use of flash distillation under reduced pressure 8a (0.21 g, 1.06 mmol, 53%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 4.12 (q, 2 H, J = 7.17 Hz), 2.30 (t, 2 H, J = 7.6 Hz), 2.03 (t, 2 H, J = 7.7 Hz), 1.63-1.57 (m, 10H), 1.45-1.22 (m, 6 H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 173.8, 127.3, 124.1, 60.1, 34.4, 34.0, 27.7, 24.9, 20.5, 20.0, 18.2, 14.2; IR (CH$_2$Cl$_2$) δ 3060 (w), 2928 (m), 2864 (m), 1726 (s), 1425 (m), 1253 (s), 1165 (w), 1115 (w) cm^{-1}; MS (EI) m/z 198 (M$^+$, 25), 110 (44), 55 (99), 41 (88), 32 (69); HRMS m/z 198.1613, Calcd for C$_{12}$H$_{15}$ (M-1) 198.1619.

8-Acetoxy-2,3-dimethyl-oct-2-ene (8b)

The crude mixture obtained from zinc-copper reagent 7b (5.0 mmol) and cation 2 (2.0 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give 8a. After purification by use of flash distillation under reduced pressure 8b (0.16 g, 0.83 mmol, 41%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 3.99 (t, 2 H, J = 6.8 Hz), 1.99 (s, 3 H), 1.58 (s, 9 H), 1.33-1.20 (m, 6 H), 0.88-0.77 (m, 2 H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 171.1, 127.6, 123.9, 64.6, 28.6, 27.9, 25.9, 20.9, 20.5, 20.1, 18.3; IR (CH$_2$Cl$_2$) 3072 (w), 2930 (m), 2862 (m), 1729 (s), 1426 (w), 1290 (w), 1240 (s), 1024 (m) cm^{-1}; MS (EI) m/z 198 (M$^+$, 20), 138 (11), 95 (91),

55 (100), 32 (32); HRMS m/z 198.1613 Calcd for $C_{12}H_{22}O_2$ 198.1619.

Ethyl 5,7-Dimethyl-6-octenoate (9a)

The crude mixture obtained from zinc-copper reagent **7a** (5.0 mmol) and cation **3** (2.0 mmol) was seperated by flash colurnn chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give **9a** and β,γ-unsaturated ketone **10a**. After purification by use of flash distillation under reduced pressure **9a** (0.11 g, 0.56 mmol, 28%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 4.86 (d, 1 H, J = 9.3 Hz), 4.11 (q, 2 H, J = 7.1 Hz), 2.31-2.18 (m, 3 H), 1.68-1.54 (m, 6 H), 1.33-1.19 (m, 6 H), 0.98-0.83 (m, 4 H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 173.8, 111.0, 60.1, 37.2, 34.5, 32.2, 25.7, 23.0, 21.2, 17.9, 14.2; IR (CH$_2$Cl$_2$) 3056 (m), 2964 (s), 1726 (s), 1448 (m), 1375 (m), 1188 (m), 1031 (m) cm^{-1}; MS (EI) m/z 198 (M$^+$, 5), 109 (10), 83 (100), 55 (42), 41 (32); HRMS m/z 198.1610, Calcd for $C_{12}H_{22}O_2$ 198.1619.

Ethyl 6,8-Dimethyl-5-oxo-7-nonenoate (10a)

After purification by use of flash distillation under reduced pressure β,γ-unsaturated ketone **10a** (0.11 g, 0.48 mmol, 24%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 4.99 (dd, 1 H, J = 9.3, 1.4 Hz), 4.10 (q, 2 H, J = 7.2 Hz), 3.34 (m, 1 H), 2.54-2.46 (m, 2 H), 1.71 (dd, 6H, J = 4.9, 1.3 Hz), 1.25 (t, 3H, J = 7 Hz), 1.10 (d, 3H, J = 6.8 Hz); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 211.4, 173.2, 134.6, 124.0, 60.2, 46.5, 39.2, 36.1, 33.3, 25.7, 18.9, 18.1, 16.4, 14.2; IR (CH$_2$Cl$_2$) 3064 (s), 2974 (s), 2932 (s), 1726 (s), 1448 (m), 1428 (m), 1376 (m), 1252 (w), 1099 (s), 1064 (s) cm^{-1}; MS (EI) m/z 226 (M$^+$, 1),180 (25),162 (9), 142 (100), 114 (99), 87 (99), 83 (99), 58 (28), 43 (99); HRMS m/z 226.1571, Calcd for $C_{13}H_{22}O_3$ 226.1568.

8-Acetoxy-2,4-dimethyl-oct-3-ene (9b)

The crude mixture obtained from zinc-copper reagent **7b** (5.0 mmol) and cation **3** (2.0 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give **9b** and β,γ-unsaturated ketone **10b**. After purification by use of flash distillation under reduced pressure **9b** (0.08 g, 0.4 mmol, 20%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 4.86 (d, 1 H, J = 9.3 Hz), 4.04 (t, 2 H, J = 6.8 Hz), 2.24 (m, 1 H), 2.05 (s, 3 H), 1.68-1.56 (m, 6 H), 1.36-1.16 (m, 5 H), 0.97-0.86 (m, 4 H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 171.2, 131.2, 129.9, 64.6, 37.4, 32.3, 28.7, 25.7, 23.8, 21.2, 20.9, 17.9; IR (CH$_2$Cl$_2$) 3058 (w), 2958 (m), 1729 (s), 1424 (m), 1275 (m), 1244 (s), 1157 (m), 1069 (w) cm^{-1}; MS (EI) m/z 198 (M$^+$, 1), 138 (18), 123 (22), 123 (22), 95 (26), 83

(100), 55 (46), 41 (31); HRMS m/z 198.1614, Calcd for $C_{12}H_{22}O_2$ 198.1619.

9-Acetoxy-2,4-dimethyl-5-oxo-non-3-ene (10b)

After purification by use of flash distillation under reduced pressure β,γ-unsaturated ketone **10b** (0.09 g, 0.4 mmol, 20%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 5.01 (d, 1 H, J = 9.3 Hz), 4.05 (t, 2 H, J = 6.1 Hz), 3.35 (m, 1 H), 2.47-2.27 (m, 2 H), 2.04 (s, 3 H), 1.74-1.57 (m, 10 H), 1.12-1.08 (d, 3 H, J = 6.8 Hz); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 211.8, 171.1, 134.5, 124.1, 64.1, 46.5, 39.7, 28.1, 25.7, 20.9, 20.1, 18.1, 16.4; IR (CH$_2$Cl$_2$) 3064 (w), 2970 (m), 2934 (m), 1730 (s), 1606 (w), 1450 (m), 1424 (m), 1369 (m), 1278 (m), 1242 (s), 1159 (w) cm^{-1}; MS (EI) m/z 226 (M$^+$, 1), 102 (79), 84 (91), 55 (57), 33 (100); HRMS m/z 226.1566, Calcd for $C_{13}H_{22}O_3$ 226.1568. The above reaction was performed under the same reaction conditions except that the addition temperature was kept at -10 °C to give 0.06 g (0.3 mmol, 15%) of **9b** and 0.19 g (0.86 mmol, 43%) of **10b**.

1,4-Dimethyl-5-phenyl-pent-2-ene (9c)

The crude mixture obtained from zinc-copper reagent **7e** (5.0 mmol) and cation **3** (2.0 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give **9c**. After purification by use of flash distillation under reduced pressure **9c** (0.20 g, 1.16 mmol, 58%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.20-7.01 (m, 5 H), 4.87 (d, 1 H, J = 8.7 Hz), 2.52-2.32 (m, 3 H), 1.55 (s, 3 H), 1.34 (s, 3 H), 0.82 (d, 3 H, J = 7.3 Hz) ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 141.2, 130.5, 130.3, 129.3, 127.9, 125.5, 44.0, 34.6, 25.7, 20.7, 17.7; IR (CH$_2$Cl$_2$) 3034 (w), 2964 (m), 2924 (m), 1604 (m), 1450 (m), 1424 (m), 1088 (w) cm^{-1}; MS (EI) m/z 174 (M$^+$, 1), 91 (15), 83 (100), 55 (49), 41 (23), 32 (81), 28 (35), 18 (23). HRMS m/z 174.1435, Calcd for $C_{13}H_{18}$ 174.1408.

6,7-Dimethyl-4-oxo-oct-6-en-1-nitrile (11)

The crude mixture obtained from zinc-copper reagent **7d** (5.0 mmol) and cation **2** (2.0 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give β,γ-unsaturated ketone **11** and a trace amount of the isoprenyl adduct (derived from teminal addition). After purification by use of flash distillation under reduced pressure **11** (0.20 g, 1.18 mmol, 59%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 3.18 (s, 2 H), 2.80 (t, 2 H, J = 7.3 Hz), 2.57 (t, 2 H, J = 8.8 Hz), 1.73-1.62 (m, 9 H); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 204.8, 129.4, 120.2, 118.9, 48.5, 36.4, 20.6, 20.4, 19.0, 11.2; IR (CH$_2$Cl$_2$) 3056 (m), 2992 (m), 2922

(m), 2250 (m), 1715 (s), 1413 (m), 1084 (m), 904 (m) cm^{-1}; MS (EI) m/z 165 (M$^+$, 11), 83 (88), 69 (14), 55 (77), 39 (16), 32 (49), 28 (100), 18 (51); HRMS m/z 165.1152, Calcd for $C_{10}H_{15}NO$ 165.1153.

5,7-Dimethyl-oct-6-en-1-nitrile (12)

The crude mixture obtained from zinc-copper reagent **7d** (5.0 rnmol) and cation **3** (2.0 mmol) was seperated by flash column chromatography (silica gel) with hexanes/EtOAc (20/1) as eluant to give **12** and β,γ-unsaturated ketone **13**. After purification by use of flash distillation under reduced pressure **11** (0.08 g, 0.52 mmol, 26%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 4.78 (d, 1 H, J = 9.4 Hz), 2.27-2.10 (m, 3 H), 1.61-1.18 (m, 10 H), 0.86 (d, 3 H, J = 3.3 Hz); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 130.9, 130.2, 119.8, 36.6, 31.9, 25.7, 23.5, 21.3, 17.9, 17.2; IR (CH$_2$Cl$_2$) 3058 (m), 2962 (m), 2924 (m), 2246 (m), 1606 (m), 1425 (m), 1379 (w), 1251 (m), 1097 (w) cm^{-1}; MS (EI) m/z 151 (M$^+$, 1), 136 (5), 84 (36), 66 (28), 52 (22), 42 (100), 38 (35), 28 (23); HRMS m/z 151.1354, Calcd for $C_{10}H_{17}N$ 151.1360.

6,8-Dimethyl-5-oxo-non-7-en-1-nitrile (13)

After purification by use of flash distillation under reduced pressure β,γ-unsaturated ketone **13** (0.07 g, 0.4 mmol, 20%) was obtained as a colorless liquid: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 4.92 (d, 1 H, J = 9.7 Hz), 3.32 (m, 1 H), 2.7-2.2 (m, 2 H), 1.67 (m, 6 H), 1.06 (d, 3 H, J = 6.8 Hz); ^{13}C NMR (CDCl$_3$, 50.5 MHz) δ 210.4, 135.3, 123.6, 119.2, 46.5, 38.0, 25.7, 19.4, 18.1, 16.4, 16.2; IR (CH$_2$Cl$_2$) 3058 (w), 2976 (m), 2934 (m), 2248 (w), 1709 (s), 1447 (m), 1415 (w), 1376 (m), 1379 (w), 1278 (w), 1006 (w) cm^{-1}; MS (EI) m/z 179 (M$^+$, 1), 83 (100), 55 (40), 49 (19), 41 (32), 28 (23), 18 (30); HRMS m/z 179.1312 Calcd for $C_{11}H_{17}NO$ 179.1310.

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